SANDIA NATIONAL LABORATORIES
CHEMICAL & DISPOSAL ROOM PROCESSES DEPARTMENT 6748
WASTE ISOLATION PILOT PLANT PROJECT

TOP-538

CALIBRATION, USE, AND MAINTENANCE OF THE MODEL 5012 CARBON DIOXIDE COULOMETER

Revision 0

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1.0 REVISION HISTORY

This document replaces TOP-6119-04 draft 2. The only reason for this revision is to comply with SNLA-WIPP QA requirements.

2.0 PURPOSE

This procedure provides for the calibration, operation, maintenance of the UIC Model 5012 Carbon Dioxide Coulometer as part of the laboratory geochemistry research activities in support of the Waste Isolation Pilot Plant (WIPP) Project.

3.0 SCOPE

This procedure is applicable only for the UIC Model 5012 Carbon Dioxide Coulometer.

This document is not meant to substitute for the manufacturer's reference manual for the Carbon Dioxide Coulometer. The user is responsible for reading and understanding the manuals (see references).

4.0 SAFETY

This document does not address ES&H issues. Laboratory ES&H procedures described in the SOPs of the laboratory in which the equipment is used shall be adhered to.

5.0 RESPONSIBILITIES

The Principal Investigator (PI), or designee, whose activities warrant the use of this procedure is responsible for implementing the requirements of this procedure.

The Project Scientist (PS), or designee, is responsible for performing the calibrations and measurements following the requirements of this procedure, documenting calibrations, and assuring that the latest revision of this document is followed.

The Quality Assurance Manager (QA Manager) is responsible for monitoring the work to assure proper implementation of the procedure and for assuring its continued effectiveness.

6.0 CONTROLS

Controls are established by written procedures or instructions prepared in accordance with QAP 5.3, PREPARING, REVIEWING, AND APPROVING TECHNICAL OPERATING PROCEDURES (Revison 1, effective date: 7/31/95) of the Sandia National Laboratories WIPP Quality Assurance Program. Procedures are issued in accordance with QAP 6.1, DOCUMENT CONTROL SYSTEM (Revision 1, effective date: 7/31/95) of the Sandia National Laboratories WIPP Quality Assurance Program.

6.1 STANDARDS

Calibration will be verified using commercially obtained carbon standards that are traceable to NIST or other nationally recognized standards. The manufacturer, lot numbers and expiration dates (if any) of the standards used shall be recorded in the laboratory notebook.

The standards will not be used past the expiration date listed on the container by the manufacturer.

6.2 GAS REQUIREMENTS

The minimum certified purity of oxygen to be used is 99.995%.

7.0 QUALITY CONTROL

All measurements must be within the instrument's linear range where interference correction factors are valid. If they are higher than the linear range covered by the correction factors, the samples shall be diluted and reanalyzed. Alternatively, a sample measurement of an analyte that exceeds the calibration range may be quantified without dilution provided that an analyte standard of higher concentration than the sample is shown to be linear.

Analyze a minimum of one method blank for every 10 samples prepared.

If results of a QC Sample are not within the control boundaries (see section 7.2), all samples bracketed by this QC sample shall be flagged on the data reports and corrective action documented with the data.

7.1 CALIBRATION

There is no means for the user to calibrate the Carbon Dioxide Coulometer. The unit was factory-calibrated and its calibration was verified by the installing technician.

Quality Control is implemented through use of performance tests.

7.2 PERFORMANCE TEST CRITERIA

Performance tests will be done by measuring the carbon content of a QC sample. A difference between the value of the measurement and the nominal value of the QC sample of great than 10% shall constitute a failed performance test (see section 7.3).

7.3 CORRECTIVE ACTION

If a performance test is failed, the setup of the instrument shall be examined and the test repeated. If it fails again, periodic maintenance as described in section 6 of the reference manual (see Appendix 2) shall be implemented, and the performance test shall then be repeated. If the performance test is failed once again, troubleshooting as described in section 8 of the reference manual shall consulted and corrective action taken as required. If the instrument still fails its performance test, it shall be tagged and taken out of service until repaired.

Failures of performance tests and the remedial action taken shall be documented on the analysis printout. Failures of more than one performance test in a given day shall be documented in the appropriate scientific notebook.

7.4 FREQUENCY

The instrument's calibration shall be verified with performance tests immediately prior to and immediately after each day's use. If a batch of analyses are done, a performance test will done once every 5 analyses.

8.0 PROCEDURE

Analyses will be performed as per instructions on pages 3 through 8 of the user's guide (see Appendix 1).

8.1 UNIT PREPARATION

Purge Model 5120 TOTAL CARBON APPARATUS overnight at 950°C and 20 cc/minute of ultra-pure O2 gas.
Clean cells with DI water.
Fill cathode cell about halfway with cathode solution.
Place about 100 mg of KI crystals in anode cell, fill to same level as cathode cell with anode solution.
Attach Tygon tube from cell to Model 5120. Keep bubbles out of light path.
Adjust %T to 100%.
Turn cell on.
Place cell in "run" mode.
Turn computer on.
Type:

CD\UIC (enter)
GWBASIC (enter)
LOAD "CARBON" (enter)
RUN (enter)

8.2 ANALYSIS

Analyses will be performed as per instructions on pages 3 through 8 of the user's guide (see Appendix 1).

9.0 MAINTENANCE

Maintenance will be performed on the instrument as instructed in section 6 of the reference manual (see Appendix 2) with the following exception:

Methanol will not normally be used to clean the frit because of waste disposal considerations. Deionized water should be used instead, unless this proves ineffective, in which case 1:1 nitric acid should be used as described on page 1 of Appendix 2.

10.0 QA RECORDS

Performance test printouts, data, as well as certificates for gases and standards use will be submitted to the SWCF *or* the results will be recorded in the laboratory notebook in accordance with Sandia National Laboratories WIPP Quality Assurance Procedure 20-2, "PREPARING, REVIEWING, AND APPROVING SCIENTIFIC NOTEBOOKS" (Revision 1, effective date: 7/31/95).

11.0 REFERENCES

Environmental Protection Agency, 1986. *SW-846, Method 9060: Total Organic Carbon,* Office of Solid Waste and Emergency Response, Washington, DC.

UIC Incorporated, 1987. *Instruction Manual - Model 5120 Total Carbon Apparatus*. UIC Incorporated. Joliet, IL.

UIC Incorporated, 1991a. *UIC's Model 5012 Carbon Dioxide Coulometer Reference Manual*, UIC Incorporated, Joliet, IL.

UIC Incorporated, 1991b. *User's Guide to the Interface IBM PC Program for the Model 5012 CO2 Coulometer*, UIC Incorporated, Joliet, IL.

APPENDIXES

APPENDIX 1: from *User's Guide to the Interface IBM PC Program for the Model 5012 CO2 Coulometer*	**Analysis**	8 pages
APPENDIX 2: from *UCI's Model 5012 Carbon Dioxide Coulometer Reference Manual*	**Maintenance**	2 pages

THE INTERFACE PROGRAM

The interface program allows the user to run sample analyses or to retrieve stored data.

The program is designed to prompt the user for all input parameters. The program functions include conducting an analysis, retrieving stored data, or exiting from the program and returning to the computer's operating system.

The program also provides for correcting any entry errors before starting an analysis. Improper entry format, e.g., attempting to enter alpha information where numeric should be, will not be excepted by the computer and and the user will be prompted to try again.

Most alpha entries require upper case, so it is convenient to set the "caps-lock" key on the computer's keyboard.

ANALYSIS ROUTINE

After the program starts and the title information is displayed, the SELECT OPTION menu appears. Select #1 to enter the Analysis Routine.

The Analysis Routine requires the operator to select Analysis Parameters before entering sample information and beginning a test. A blank determination is optional before any analysis.

I. ANALYSIS PARAMETERS

A. Analyst I.D.

Up to five (5) alpha-numeric characters are allowed for an analyst identification. Error messages will be displayed if more than six charcters are used or if NO entry is made.

B. Analysis Type

There are six (6) choices for analysis type. The analysis type selected will determine the chemical units used for the final result calculations, and, which sample size will be allowed. After a selection is made, the screen will remind the user to set the MODE switch on the Coulometer to the one which best corresponds with the selected analysis type.

Select the desired analysis type by entering the corresponding number. An improper entry will prompt the user for a correct entry.

A summary of the ANALYSIS TYPES is given below.

1. Carbon (C) - The C analysis will report results either as ppm C or %C. Sample size information will be queried for either weight or volume units. The MODE should be set for ug C (#1 or 2) for this analysis type.

2. Carbon Dioxide (CO2) - The CO2 analysis will report results either as ppm CO2 or as %CO2. Sample size information will be queried for either weight or volume units. The MODE should be set to ug CO2 (#4) for this analysis type.

3. Carbon Trioxide (CO3) - The CO3 analysis will report results either as ppm CO3 or %CO3. Sample size information will be queried for either weight or volume units. The MODE should be set to ug CO3 (#5) for this analysis type.

4. Carbon in Water (CW) - The CW analysis is for the high temperature combustion analysis and a 200 ul sample size. The MODE should be set to mgC/L (#3) for this analysis type. Results will be reported as mg C/L or %C.

5. Surface Carbon (SC) - The SC analysis will report results as mg C/m2. The sample size information will be queried for measurement units. The MODE should be set to ug C (#1 or 2) for this analysis type.

6. Oxygen (O) - The O analysis is for the oxygen analysis configuration and reports results as either ppm O or %O. The sample size information will be queried for either weight or volume units. The MODE should be set to ug O (#6) for this analysis type.

C. Sample Size Information

If CW is the selected analysis type, a 200 ul sample size is ASSUMED and no sample size options are requested.

If SC is the selected analysis type, the user will be asked to select inches or millimeters as the MEASUREMENT UNITS. The number corresponding to the desired measurements units should be entered.

For all other analysis types, the operator must select either Weight or Volume units, by entering 'W' or 'V'. Specific weight or volume units will then be requested.

Weight unit choices include grams (g), milligrams (mg) or micrograms (ug). Volume units are either milliliters (ml) or microliters (ul). Enter the number corresponding to the desired units.

D. Timing Type

Either the COULOMETER or the COMPUTER can control the timing for an analysis.

When the COULOMETER is used for timing, the coulometer sends a reading each time the interval on the TIME SET is reached. The NUMBER OF READINGS requested by the program, is the minimum number of reading that will consistute a test.

When the number of readings sent by the coulometer equals the number of readings entered in the program, the difference between last TWO readings taken is calculated. If that difference is less than the Difference Criterion (percentage) of the LAST reading, the test is considered complete and the final results are calculated. If the difference is more than the difference criterion of the last reading, additional readings are taken until the difference between the last two readings IS less than the allowed criterion.

COMPUTER timing asks the analyst for a specific analysis and interval lengths. When the entered analysis length has been reached, the analysis is complete, even if the coulometer titration is not complete (no difference criterion is used). This timing type is only intended for special TIMED analysis work.

Select the timing type by entering the appropriate number. If Coulometer timing (#1) is requested, enter the Number of readings desired to constitute a minimum test time (minimum number of readings is 3). When Computer timing (#2) is selected, enter the desired analysis length and increment length (time between readings) in minutes. Fractions are allowed for COMPUTER timing.

E. Factor

The FACTOR is a multiplier used in the final calculation. It will most often be 1. It is designed to allow for conversion of the final calculations into units not avaliable on the coulometer MODE switch, or, to reflect sample dilution.

> Example: The user is testing the purity of calcium carbonate and wants the final units as a %CaCO3, the coulometer MODE can be set for ug C (#2) and the FACTOR entered as '8.334'. (Each ug C is equivalent to 8.334 ug CaCO3.)

The chemical units printed in the final result will reflect the analysis type chosen, and are not altered by the FACTOR.

F. Blank

The BLANK is the instrument 'backround'. The blank value is equivalent to the coulometer display reading at the entered analysis length. (For Coulometer timing, the analysis time is equal to the number of readings entered in this program multiplied by the interval length set by the TIME SET on the coulometer.)

This interface program allows you to run blanks at any time during a series of analyses. The Blank Routine is described in a later section.

A numberic value for the blank must be entered whether the blank routine is run or not.

G. Data Storage Option

The operator has the option to store analysis data (Y or N) on a disk. If data storgae is selected, a FORMATTED disk should be inserted into DRIVE B.

All sample information and all data readings are stored, if storage is requested, at the completion of an analysis run. The operator is required to periodically check the storage space available on the disk, as the program does not keep track of the amount of storage available, and will lose any data that will not fit on to the end of a disk.

Information on the data storage format is given in the DATA STORAGE section.

H. Difference Criterion

The Difference criterion is a percentage value used when determining the end of an analysis with COULOMETER timing. The default value for the difference criterion is 0.1%. If the user desires to change this value, it can be accessed in the Change Routine.

If changing the difference, the new criterion value should be entered as a percentage.

> Example: If the new difference is to be 0.5%, enter the new value as '0.5'.

II. SAMPLE INFORMATION

A. Sample

Up to six (6) alpha-numeric characters are allowed for a sample identification. The same number can be used for multiple analyses.

An error message will be displayed if more than six characters are used, or, if NO entry is made.

B. Sample Size

Sample size queries are requested for all analysis types except for CW and the BLANK routine. Required enteries are queried by the size units entered in the ANALYSIS PARAMETERS.

A sample size can not be defined by zero for a non-blank routine analysis.

III. BLANK ROUTINE

When the user chooses to run a blank, the program assigns the sample # as 'Blank' and the sample size as 0. This sample information can not be changed.

A blank run will finish after analysis time entered in the analysis parameters has been reached. (Analysis time is the Analysis Length for Computer timing and the Number of Readings for Coulometer timing.)

After a blank run finishes, the blank value determined by the run is printed on the analysis report and the user has the option to run another Blank. If an additional run is not made, a numeric blank value entry will be requested.

IV. STARTING AN ANALYSIS

After successfully entering the sample information (or opting for a blank run), the user has the option to either begin the analysis, or, to enter the Change Routine (described later).

To begin (run) the analysis enter an 'R'. The program will reset the coulometer and print the heading of the analysis report. Data readings will be printed as they are collected until the analysis is finished, or interrupted by the user.

V. CHANGE ROUTINE

If an Analysis Parameter needs to be changed, or if an error was made on sample entry, the user can enter the Change Routine to correct the entry.

Enter a 'C' to enter the Change Routine.

A numbered list of analysis parameters will be displayed. To change a parameter, select the number in front of the desired parameter. Some parameter changes are not always allowed. Messages will appear if an illegal selection has been made.

To exit the Change Routine and begin the analysis run, enter the number corresponding to the start the run command.

VI. INTERRUPTING AN ANALYSIS

An analysis can be interrupted by the user by depressing "S" on the keyboard at any time during the test. The test will terminate when the next reading is taken from the coulometer.

If an analysis is interrupted, the report shows that the run was aborted and no final calculations are made.

VII. CALCULATIONS

When an analysis has finished (without being aborted by the operator) the calculations are completed and the final results printed on the analysis report.

The calculations for the Analysis Types are as follows:

1. CW - In Mode #3 (mgC/L), the sample size of 200ul is already in the calculations ('mgC/L' is equivalent to ' ugC/0.2ml'). The final result for CW is calculated as:

$$(R - (B/N*G)) * F$$

where:

R = Last Coulometer display reading as mgC/L units
B = Blank entered as mgC/L units
N = Number of Readings entered
G = Number of Readings taken
F = Factor

If the final result is greater than 10,000 mgC/L, the final result is converted to a percentage.

2. SC - For SC the final result is always reported as 'mgC/m2'. The final result for SC is calculated as follows:

$$((R - (B/N*G)) * F) / H$$

where:

R = Last Coulometer display reading as ug C
B = Blank entered as ug C
N = Number of Readings entered
G = Number of Readings taken
F = Factor
H = Sample Area = L * W * S * 2
L = Sample strip Length
W = Sample strip Width
S = Number of Sample strips
2 = 2 sides of sample strips

Unit conversions for the sample size are completed by the program.

3. All other Analysis Types calculate final results either on a weight basis or a volume basis.

The final results are calculated as follows:

$$((R - (B/N*G)) * F) / S$$

where:

R = Last Coulometer display reading in 'Z' units
B = Blank entered in 'Z' units
N = Numbers of Readings entered
G = Number of Readings taken
F = Factor
S = Sample Weight or Volume

'Z' units are either micrograms (ug) C, CO2, CO3 or O - corresponding to the selected analysis type.

All unit conversions for sample size are completed by the computer.

If the result is greater than 1000 'ppm', the result is converted to a percentage. For Weight based calculations, ppm = 'ug/g', and, for volume based calculations ppm = 'mg/L'.

VIII. AFTER AN ANALYSIS IS COMPLETE

When an analysis is complete, a SELECT OPTION display appears. The user can select to run another analysis of the SAME type, a DIFFERENT type, a BLANK analysis or to Quit.

If the SAME type of analysis is to be repeated, the user is prompted to enter the next Sample # and Sample Size.

If a DIFFERENT analysis type is selected, the program will go back to the begining and all analysis parameters must be entered for the new analysis type.

Choosing the BLANK analysis sets the sample # to Blank and prompt the user to begin the blank run.

Quit will exit the analysis portion of the program and go back to the original option screen.

SECTION 6: Preventative Maintenance

INTRODUCTION

This section includes information on routine maintenance of the Model 5012 CO_2 Coulometer, as well as a list of parts and chemicals that should be maintained to keep your coulometer operating satisfactorily.

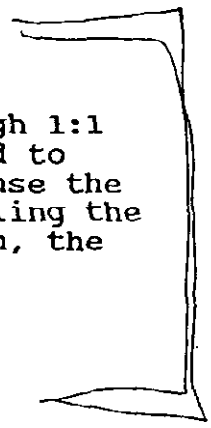
DAILY MAINTENANCE

Care should be taken to avoid spilling any substance on the coulometer that could damage the electronics or casing. In general, the only daily maintenance is to change the coulometer cell solutions. At the end of use for the day, the cell clean-up should follow this procedure.

1. Turn off the cell current switch and the main power supply switch.
2. Unplug the electrodes, loosen the gas inlet tube and the gas exit vent line from the rear of the cell compartment, and remove the cell from the cell holder.
3. Dispose of the cell solutions according to local and Federal regulations.
4. Rinse the cell and both electrodes thoroughly with water.
5. Clean the glass frit between the cathode and anode compartments in the cell by vacuum pulling methanol through the frit, followed by distilled water. This is done by attaching a water aspirator to a water supply, and the tubing from the side leads to a stopper which fits the anode compartment. Methanol is placed in the cathode compartment and the water is turned on, pulling the methanol through the frit. Repeat with distilled water.
6. Rinse the cell with distilled water and dry to remove excessive amounts of water.
7. Store the cleaned cell assembly in the cell holder to avoid breakage of the cell components.

THOROUGH CLEANING

At times, component parts may require a more thorough cleaning. To clean the frit, fill the cell with enough 1:1 nitric acid:water to cover the frit and allow the acid to clean the frit overnight. Dispose of the acid and rinse the cell completely with water before reuse. After refilling the anode compartment, if the potassium iodide turns brown, the frit has not been sufficiently rinsed.



If the platinum electrode appears tarnished, deposits have formed. This can be prevented by not leaving the cell assembly filled and unused overnight, or for extended periods of time. To remove the deposits, soak the electrode in 1:1 nitric acid:water for a few hours. Rinse thoroughly before reuse.

SHORT TERM SHUT DOWN

If you need to be away from the coulometer for short periods of time during the day (lunch, for example), it is good practice to disconnect the inlet gas flow line from the check valve in the rear of the coulometer. This action prevents the coulometer solution from being siphoned out of the cell.

AUDIBLE SIGNAL DISCONNECTION

The Model 5012 CO_2 Coulometer is equipped with an audible signal. A beep will sound at each time interval determined by the time set switch. To disable the signal, open the right side of the cabinet and disconnect the lead wires attached with a molex plug to the microprocessor board of the coulometer. Additional information regarding the microprocessor board and its location can be found in section 9, "Electronic Service Information".

RECOMMENDED SPARE PARTS AND REAGENTS

Some spare parts and reagents are recommended as an inventory to assure continuous operation of the Model 5012 CO_2 Coulometer. The parts and chemicals suggested are as follows.

PART NUMBER	PART DESCRIPTION
192-003	Check valve, disposable, pkg. of 6
210-015	Cell assembly, Model 5012
Includes all of the following:	
101-033	Silver electrode
101-135	Platinum electrode
121-001	Stir bar
190-002	Gas inlet tube
119-027	Cell top, Model 5012
119-028	Anode top
200-051	Cell with fritted side arm
310-001	Coulometer cell reagents
Includes all of the following:	
300-001	Cathode solution, 1 gallon
300-002	Anode solution, 8 ounces
300-003	Potassium Iodide, 50 grams

A set of coulometer reagents normally lasts approximately 40 days. Replacement reagents should be ordered when those currently in use are 3/4 spent.